



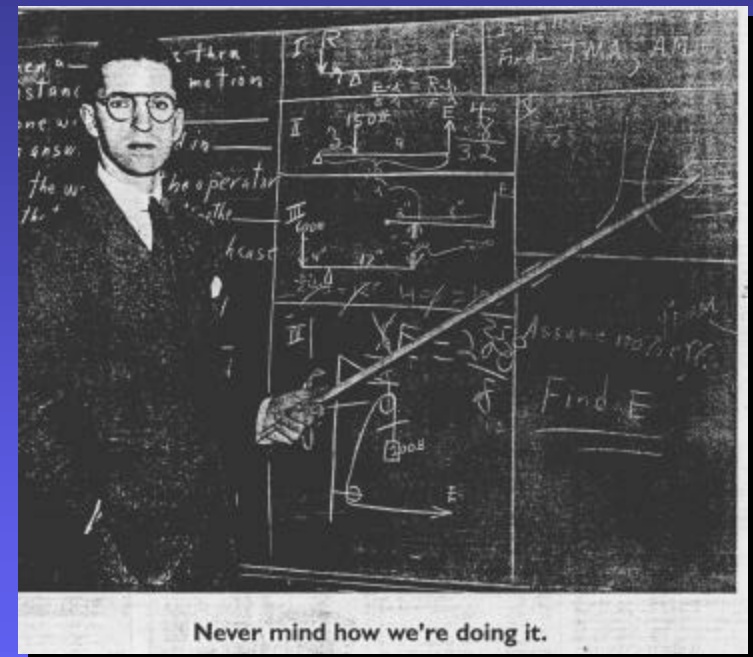
Storage Reliability of Reserve Batteries

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At Issue

- Items developed for munitions have a 20-year shelf life requirement over a wide temperature range
- Developers need to “prove” storage reliability
 - Actual documentation preferred
- Science can be difficult, time-consuming, and costly





Reservoir Evolution

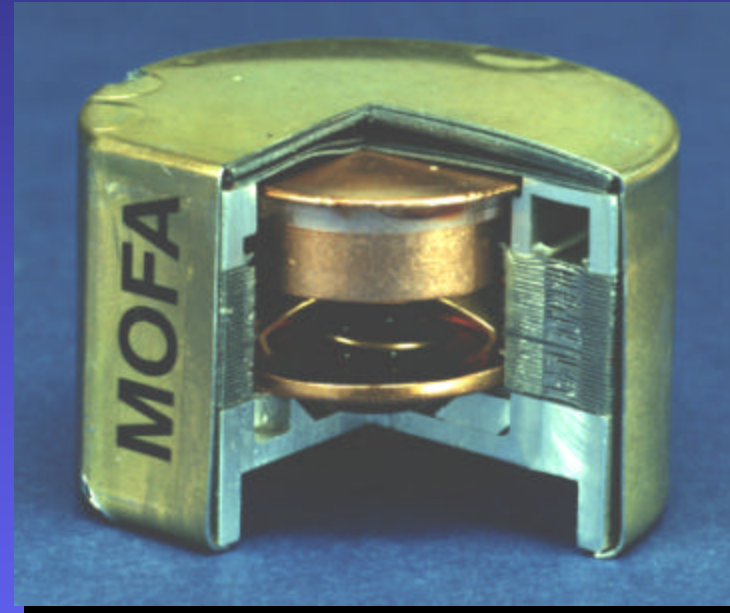
- **Army and Navy used $\text{Pb}/\text{HBF}_4/\text{PbO}_2$ reserve batteries with glass reservoirs**
- **Over time it was discovered that batteries became more sensitive to activation when dropped**
- **Glass was being attacked by the aqueous electrolyte**
- **Drove change to copper dash-pot design**



Reservoir Evolution



PS112 Ampoule



**ARL MOFA battery
(sectioned)**



A Common Approach

- **Put samples in high-temperature storage**
 - **Rule-of-Thumb: reaction rates double with every 10°C increase**
 - **1 year at 65°C = 16 years at 25°C**
- **Periodically pull samples and test battery performance**
- **Analytical work kept to a minimum**



Potential Drawbacks

- Previous slide predicts aging at 25°C
- How to accelerate aging at high temp conditions?
 - Increase beyond 74°C (165°F), but risk introducing new effects or reactions
 - Increase study time
- Might miss subtle changes that indicate trouble
- Might mask problem altogether

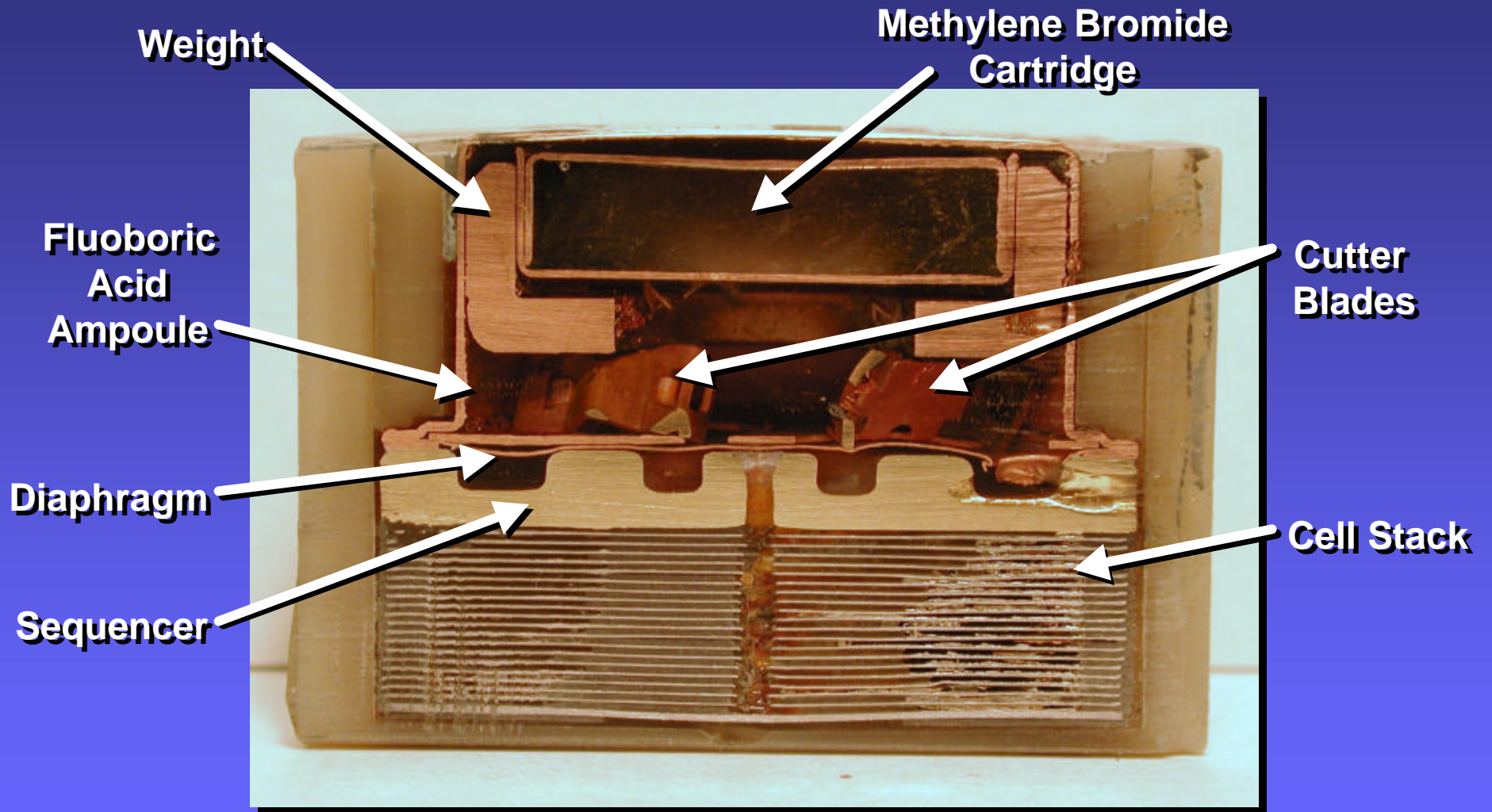


PS115: A Case Study

- **Dual-fluid, copper reservoir design**
 - **Fluoboric acid electrolyte**
 - **Methylene bromide (non-conductive, more dense)**
 - **Sequenced release of fluids**
- **Developed in 1964, used in M732 fuze starting in 1978**
- **Initial studies of reservoir/electrolyte materials indicated they were compatible**
- **Accelerated aging at 71°C (160°F) indicated no problem**



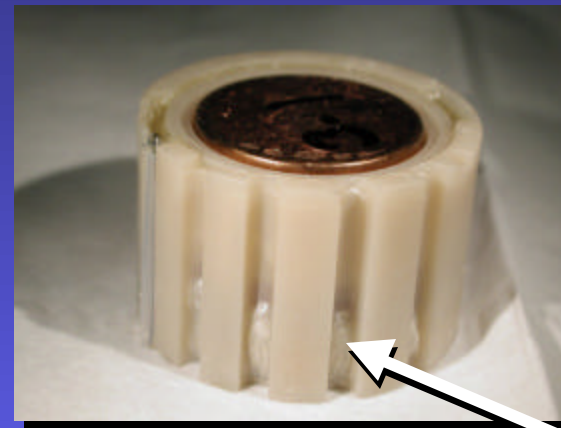
PS115 Section





PS115: Problems Detected

- Production began in 1978
- Five years later, leakage was noticed in engineering samples at HDL
- Further investigation revealed that virtually every lot produced prior to Nov 1980 contained leaking batteries





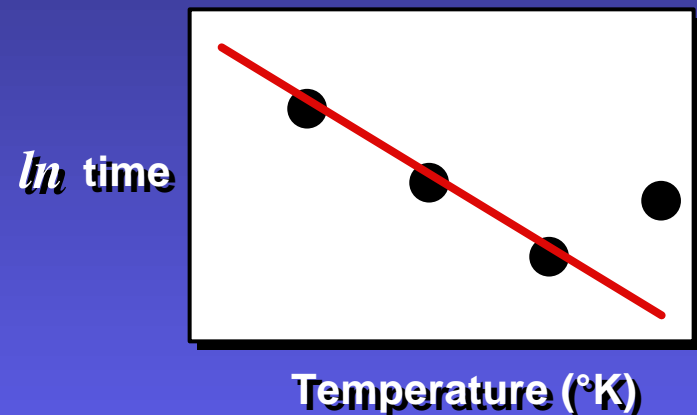
PS115: Investigation Results

- **Leakage started earlier and affected a larger percentage of units as temperature increased up to about 60°C (140°F)**
- **Beyond 60°C, incidents of leakage decreased sharply, essentially reaching zero at about 71°C (160°F)**
- **Methylene bromide fueled a complex series of reactions with the other reservoir materials**
- **Above 71°C, increased solubility of copper salts prevented the unique circumstances that caused pitting corrosion and leakage**
- **High-temp bake-out of reservoir was initial “cure”**



A Better Approach

- Store at at least three temperatures
 - determine reaction rates
 - detect changes in behavior
- Use analytical chemistry and optical techniques to measure physical changes
- Determine what is happening, and how fast





Change in Chemistry

- **Lead is pretty much history in munitions batteries**
 - **Environmental concerns, lack of business**
 - **Non-availability of some critical materials**
- **Lithium Oxyhalides are systems of choice**
 - **Good history with single-cell, glass reservoir (barrier munitions, M762 time fuze)**
 - **Starting to see metal reservoirs in artillery applications (MOFA)**
 - **Missiles use metal reservoirs**
 - **10-year shelf life?**
 - **Treated better?**



Concerns with Oxyhalide Electrolytes

- Very few materials are compatible
- *Extremely* moisture sensitive
 - Reaction products include HCl, SO₂, Cl₂, H₂SO₄
- Some additives/constituents can cause problems
- Can also be affected by light and heat
- Issues have been raised on several current programs
 - Solid forming in electrolyte?



From the Literature

- ***Generally speaking***, several metals exhibit good corrosion resistance to neutral electrolytes (LiAlCl_4 in thionyl chloride and sulfonyl chloride)
- Using AlCl_3 creates a much more corrosive environment (acid electrolyte)
- Of concern in metal containers:
 - heat-treated (welded) areas
 - stressed areas
 - crevice regions
 - metal couples



Some Lessons

- **General information is nice, but best to evaluate specific designs**
- **Great care is required to collect and prepare samples for analysis**
- **Electrolyte additives should be thoroughly studied prior to implementation**



Recommendations

- **Start thorough compatibility studies as early as possible, using representative hardware**
- **Assume studies will take some time and careful planning and execution; quick results likely to be bad news**
- **Need to understand potential failure mechanism(s): PS115**



ARL's Contribution

- **Retain in-house Government expertise**
- **Support contractor's development efforts**
- **Conduct complementary testing and analysis**
- **Work to ensure the product meets the Government's requirements**
 - **Need to independently assess the proposed technology**
 - **Government needs to be an educated buyer**